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PREPARATIVE TRAPPING OF TERT-BUTOXY RADICALS BY CAPTODATIVE OLEFINS[1,2,3]

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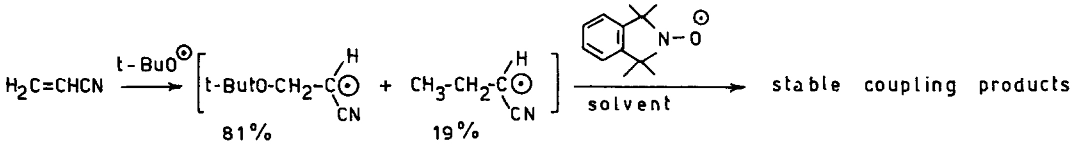
Summary : tert-Butoxy radicals generated either thermally or photochemically are trapped preparatively by various captodative olefins.

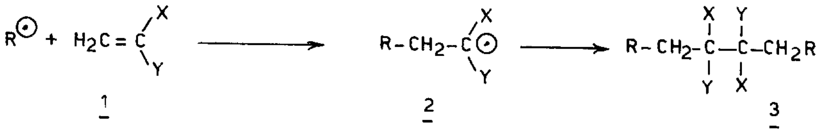
ESR spectroscopy has proven to be a valuable tool in examining the kinetics and reaction mechanism in general[4]. These studies have revealed unusual preference of tert-butoxy radicals for allylic hydrogen abstraction and their reluctance to add to monoolefins[5-8].

On the other hand, addition of tert-butoxy radicals becomes competitive or may even predominate in the case of cyclopentadiene, norbornene and norbornadiene[9]. Tert-butoxy radicals cannot be detected by ESR[10], but their mostly short lived spin-adducts can be observed using various spin-traps, e.g. tert-butyl nitrone, nitroso-tert-butane[11], various methylated pyrroline oxides[11,12] and tert-butylisocyanide[13].

However powerful the ESR technique may be, it suffers from severe limitations since the arising spin-adducts cannot be separated preparatively and must be analyzed spectroscopically as a mixture. The use of stable nitroxide radicals as co-reagents is therefore one of the major recent contributions to the study of radical additions and of polymerisations[14,15]. They lead to stable non-radical products which can be separated by TLC or HPLC techniques and then analysed. Most interestingly, however, this approach has revealed that under homosolvolytic conditions with nitroxides as solvents, acrylonitrile adds tert- butoxy radicals in 81% yield together with the 19% methyl radical adduct:



Our independent approach to trap various radical species takes advantage of pronounced radicophilic properties of captodative (cd) olefins 1[16,17]. The arising cd radical adducts 2 are sufficiently stabilised to undergo selective dimerisation leading to adduct-dimers 3 :

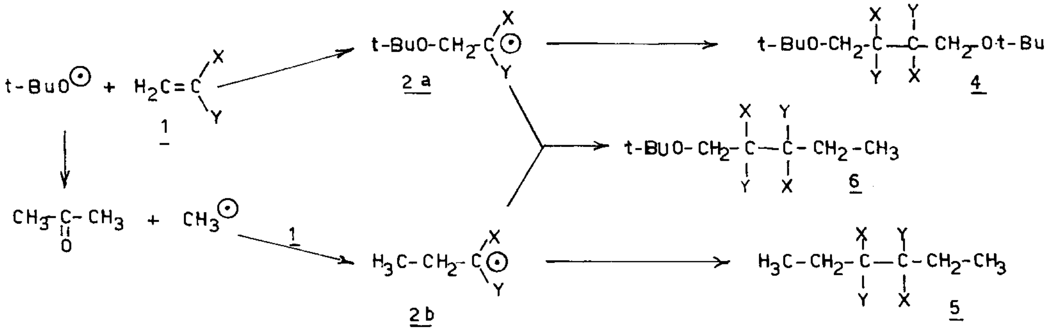


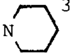
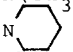
X = electron acceptor , Y = electron donor

In this study we generated the elusive and strongly electrophilic tert-butoxy radicals in the presence of a series of cd-olefins 1. As with other electrophilic carbon-centered radicals e.g. $HC^{\odot}(CO_2CH_3)_2$, 1a (X=CN, Y=S-t-Bu) does not trap tert-butoxy radicals originating from ditert-butoxylperoxide (DTBP) at 140°. Only methyl radical adduct 5a, R=CH_3 is obtained in 32% yield[17]. Since the fragmentation of tert-butoxy radicals to methyl radical and acetone is temperature dependent (Ea ∿ 13 Kcal/mole)[18], 11% of tert-butoxy radical adduct 4a besides 48% of 5a are formed at 60° using ditert-butyl peroxalate DTPO as radical source. Whereas the easily oxydizable α-methylthioacrylonitrile gave only tars, α-phenylthioacrylonitrile affords 21% of 4b while the corresponding methyl radical adduct 5b is still formed (41%). The less electron poor α-phenylthiostyrene 1c turned out to be the best trap for thermally generated tert-butoxy radicals leading to a 74% yield of a single adduct 4c.

Compared to acrylonitrile-thioethers 1a,b the more strongly nucleophilic captodative aminoanalogs 1f-h and also the ester 1e can be anticipated to react better with tert-butoxy radicals. However, these have to be generated photochemically at 20° in order to avoid the induced decomposition. Under these conditions, fair to good yields of adduct dimers 4e-h are obtained.

The low yields of adducts 4a,b,d show that cd-olefin ethers or thioethers are less efficient traps for tert-butoxy radicals than the more electron rich cd-enamines. These qualitative interpretations show that the electronic and polar effects play the key role in radical additions via SOMO-HOMO or SOMO-LUMO interactions[23] One can devise efficient traps for specific radicals by properly choosing the **c** and **d** groups. In order to assess the orbital energies of captodative olefins, XPS (ESCA) spectra of 1 were interpreted[24] and EHT calculation were performed[25]. Both sets of results will be published elsewhere.



1	X	Y	Conditions	4(%)[20]	M.P(°C)	5(%)
a	CN	S-t-Bu	DTBP[a)],140°C,12h	-	-	32[17]
			DTPO[b)],60°C,8h	11	106	48[c)]
b	CN	S-Ph	"	21	146	41[19]
c	Ph	S-Ph	"	74	152	-
a	CN	S-t-Bu	DTBP[b)],20°C,hν	26	106	-
b	CN	S-Ph	"	22	146	-
d	CN	O-CH_3	"	21	123	>5
e	CO_2CH_3		"	30	oil[21]	-
f	CN	$N(CH_3)_2$	"	59	118	-
g	CN		"	64	154	-
h	CN		"	73	181	-

a) 0.28M solution of 1a in benzene, olefin/peroxide=2:1, sealed tube

b) 0.1M solution of 1 in benzene, ratio 2:1; c)6a is also obtained in 7% yield[22].

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19.5b : meso-form ; M.p. 158° ; ^{1}H-NMR (CDCl$_3$) : δ=1.26(t,6H) ; 2.0-2.3(m,4H) 7.2-7.4(m,6H) ; 7.7(m,4H)

20.10 mmol 1, 0.73g (5mmol) DTBP in 150ml C_6H_6 are irradiated by a 150W high-pressure Hg-lamp at 20°. Products are purified by chromatography on SiO$_2$ (4a-d) or alumina (4e-h). Unless indicated otherwise, only one form probably the meso, is obtained.

4a two diastereomers : δ=1.24(s,18H) ; 1.56(s,18H) ; 3.75(d,2H) ; 4.05(d,2H) J_{gem}=9.8Hz and 1.22(s,18H) ; 1.58(s,18H) ; 3.67(d,2H) ; 3.97(d,2H) J=9.9Hz

4b : δ=1.20(s,18H) ; 3.85(d,2H) ; 3.95(d,2H) J=10.1Hz ; 7.3-7.45(m,6H) ; 7.83(m,6H) ; 7.83(m,4H)

4c : δ=0.96(s,18H) ; 4.19(s,4H) ; 7.0-7.3(m,20H)

4d two diastereomers : δ=1.23(s,18H) ; 3.54(s,6H) ; 3.70(d,2H) ; 3.76(d,2H) J_{gem}=10Hz and 1.32(s,18H) ; 3.60(s,6H) ; 3.78(d,2H) ; 3.84(d,2H) J_{gem}=10Hz

4e two diastereomers : δ=1.08 and 1.12(2s,18H) ; 1.4-1.5(m,12H) ; 2.4-2.5 (m,8H) ; 3.2-3.5(m,4H) ; 3.53 and 3.56(2s,6H)

4f two diastereomers : δ=1.23(s,18H) ; 2.53(s,12H) ; 3.87(s,4H) and 1.21 (s,18H) ; 2.56(s,12H) ; 3.74(d,1H) ; 3.84(d,1H)

4g two stereoisomers : meso 1,25(s,18H), 1.4-1.65(m,12H), 2.9-3.0(m,8H), 3.98(d,2H), 4.01(d,2H) dl : 1.26(s,18H) ; 1.4-1.65(m,12H) ; 2.9-3.0(m,8H) J_{gem}=10.1Hz 3.91(d,2H), 3.97(d,2H) J_{gem}=9.3Hz

4h : 1.26(s,18H) ; 3.0(m,8H) ; 3.6(m,8H) ; 3.93(s,4H)

21.Non-optimised, as methyl α-piperidinoacrylate 1e was available in only low amounts from methyl α-chloroacrylate and piperidine in benzene : 0.1 mol of dry piperidine are added to 0.05 mol of α-chloroacrylate in 200ml dry benzene during 4 hours at 0° and the stirring is continued overnight at 20°. Water (20ml) is then added and the organic phase is dried over K$_2$CO$_3$. Distillation gives a 5-10% yield of 1e. B.p. 70°/0.7mmHg. The main product is the corresponding Michael adduct, methyl α,β-dipiperidinopropionate.B.p. 130°/0.2 ^{1}H NMR of 1e : δ=1.47-1.62(6H), 2.62-2.80(4H), 3.78(3H), 4.43 and 4.98ppm (2s,2H)

22.6 threo and erythro ; M.p. 107-8° ; δ=1.23 ; 1.25(2s,9H) ; 1.3-1.5(m,3H) ; 1.56(s,18H) ; 2.0-2.7(m,2H) ; 3.6-4.2(m,2H)

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